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Notes on the bleaching action of light on colouring matters.—By ALEXANDER PEDLER, F.R.S., &c.

[Read, 6th Feb.]

That many colours fade when exposed to sunlight is a fact which is only too frequently observed, and which admits of no doubt. The colours which are thus bleached are almost invariably of organic nature, while coloured substances of inorganic character are, as a rule, practically unaffected by the action of light. The exact cause of this bleaching action of sunlight on organic colouring matter is, however, not well understood, and the experiments summarized in this note were conducted to add to the sum of our knowledge on this subject. They are, therefore, published not with the hope that they will set the question of the cause of the bleaching action of light at rest, but rather because they strengthen the conclusions which appear to have been arrived at by previous workers on this subject, and to exist in a more or less indefinite form in chemical literature.

That the subject of the bleaching of colours by light is not yet in a satisfactory condition may be judged by the following quotation from a work published as recently as 1890, by Professor E. Hjelt of Helsingfors, the well known Sweedish chemist, who in his work on "General Organic Chemistry," in the chapter on the "Chemical Action of Light," writes*:—

"A considerable number of organic colouring matters lose their colours and become bleached by the action of sunlight; the process by

* General Organic Chemistry, by Hjelt. Translated by Dr. Tingle, 1890.

which the colours are destroyed is unknown. The action of light upon sensitive organic substances has been little investigated generally, but a number of single observations of an interesting nature have been lately made on this subject," etc. Hence it would appear there is still room for further experimentation on this subject.

The bleaching effect of sunlight or diffused light on colours or coloured fabrics, may be due to several causes. These causes may, perhaps, be summarized as follows :—

1. The bleaching may be due to a decomposing action of the light itself, unaided by any chemical action of the oxygen, carbon dioxide, moisture, ozone, etc., present in the air, or even, though not at all probable in the great majority of cases, the loss of colour may be due to the colouring matter itself being volatile.

2. The bleaching may be caused by the light inducing some chemical action due to the oxygen, carbon dioxide, moisture, ozone, etc., of the air.

3. Or in the case of dyed colours, the bleaching may be due to some action between the organic matters of the fabrics, and the colouring matters under the influence of light, or to a similar action accompanied by a chemical action due to the oxygen, carbon dioxide, moisture, etc., contained in the air.

4. Also the bleaching action may be due to changes connected with the growth of certain low forms of life, such as germinate when bodies in a favourable condition are freely exposed to ordinary air, in which such germs of life practically always exist.

To test these propositions early in 1891, the following sets of experiments were started.

A series of six colouring matters representing roughly different parts of a spectrum was taken. The colours were Purple as represented by neutral Litmus, Blue by Methyl Blue, Green by Methyl Green, Orange by Methyl Orange, Pink by Eosine, and Red by Rosaniline Acetate. Solutions of these substances were taken of definite strength (4 grams in a litre of water), so that they could be always reproduced when required. With these solutions specimens of pure cotton-wool as representing organic matter such as used in various dyed fabrics, and asbestus, representing an inorganic surface, which would have no practical chemical action on colouring matters, were dyed, and afterwards carefully dried. With these three sets of materials, *i.e.*, the solutions, the dyed cotton, and the dyed asbestus, the following principal sets of experiments were made :—

A. The solutions were placed in tubes stoppered merely with cotton-wool, and were then exposed freely to the action of the air and

of any germs floating in the air at the time of preparation, and they were placed (*a*) one set in direct sunlight, (*b*) one in diffused daylight opposite a window with a north aspect, and (*c*) one set in perfect darkness. Fifteen experiments of this kind were started.

B. A set of solutions was taken as in A, except that the tubes containing the solution were thoroughly boiled for from 15 to 20 minutes in order to kill any germs likely to produce any action. While the solutions were still boiling the tubes containing them were plugged well with cotton-wool. Sets of these tubes were also exposed in parallel series (*a*) in direct sunlight, (*b*) in diffused daylight, and (*c*) in darkness. Eighteen experiments of this class were started.

C. Sets of the solutions were placed in tubes drawn out at one end and connected with the Sprengel mercurial pump. The solutions were boiled for 15 to 20 minutes, so as to free them from all dissolved oxygen and from all living germs, etc., and they were then completely exhausted of air and hermetically sealed. Sets of the solutions in these tubes were exposed (*a*) in full direct sunlight, (*b*) in diffused daylight opposite a north window, and (*c*) in total darkness. Eighteen experiments of this class also were started.

D. Specimens of cotton-wool, dyed with solutions of the six colours and then thoroughly dried at 100° C, were placed in test tubes, plugged at their mouths with cotton-wool, and then while thus freely exposed to air in its ordinary hygrometric condition, they were placed (*a*) in direct sunlight, and (*b*) in total darkness. Twelve experiments of this class were started.

E. Sets of dyed cotton-wool dried at 100° C, were placed in tubes rendered vacuous by the Sprengel pump, and then hermetically sealed and exposed (*a*) to direct sunlight, and (*b*) in total darkness. Twelve experiments of this class were started.

F. Specimens of asbestus were freed from organic matter and from any organisms, etc., by ignition, and dyed with the colours and carefully dried at 100° C. Specimens were placed in test tubes freely exposed to the air in its ordinary hygrometric state, and plugged with cotton-wool only. These were placed one set (*a*) in full direct sunlight, and (*b*) in total darkness. Ten experiments of this class were started.

G. Similar sets of asbestus specimens dyed with the colours and dried, were placed in tubes carefully exhausted by the Sprengel pump and hermetically sealed. One set was placed (*a*) in full direct sunlight, and a second set (*b*) in total darkness. Twelve experiments of this class were started.

The above sets of experiments were allowed to continue for periods varying in some cases up to nearly three years. In addition also some

sets of experiments were tried in which coloured substances were exposed to the action of sunlight after being moistened with water, and the bleaching under these circumstances compared with that produced by sunlight when the coloured bodies were kept free from water and only exposed to moist air. In all cases the presence of evaporating water rendered the bleaching *much* more rapid.

It will be seen that in the above list, A to G inclusive, no less than 97 experiments were started, and in addition to these a good many others were made, which are not reproduced in detail. Each experiment was examined every few days at first, and later on every few weeks, and the condition of the specimens was compared with freshly prepared specimens when necessary, and the results carefully recorded. Hence a large mass of facts was obtained. It will be seen that it would be impossible to describe the detailed results of each individual experiment, as this would take a large amount of space, nor indeed are the results of sufficient value to make the publication of the details necessary. Hence the main results only of the experiments are summarised in seven tables, A to G, which are printed below.

It may be convenient here to explain that the comparative results shown in tables A and B, are intended to differentiate between the causes referred to in 4 previously. The comparison of the results in B and C, is intended to differentiate between the causes referred to in 1 and 2. The comparison of the results given in D and E, and given in F and G, is again intended to differentiate between the causes referred to in 1 and 2, and finally the results of D and E together, compared with those of F and G together, will enable a conclusion to be obtained with reference to cause 3.

A. *All colours in solution in water, placed in test tubes without boiling, and simply closed with a plug of cotton-wool.*

Colour used.	In Total Darkness.			In diffused Daylight, opposite a North Window.			Exposed daily to direct Sunlight.		
	2 months after.	10 months after.	14 months after.	2 months after.	10 months after.	14 months after.	2 months after.	10 months after.	14 months after.
Litmus ...	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached slightly more purple.	Unbleached slightly more purple.	Began to bleach after few days, in 2 months quite bleached.	Bleached.	Bleached.
Methyl Blue ...	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Partially bleached.
Methyl Green ...	”	”	”	”	”	”	Partially bleached.	No green colour left, solution blackish.	No green colour left.
Methyl Orange ...	”	”	”	”	”	”	Unbleached.	Result inconclusive.	Experiment lost.
Eosine ...	”	”	”	”	”	”	Partially bleached.	Considerably bleached.	Almost colourless.

B. *All colours in solution in water; solutions boiled for* 15 *minutes and while boiling the tube closed with a cotton-wool plug. Therefore the liquids had been to a great extent freed from germs, etc.*

Colour.	In Total Darkness.			In diffused Daylight opposite a north window.			Exposed daily to direct Sunlight.		
	2 months after.	10 months after.	14 months after.	2 months after.	10 months after.	14 months after.	2 months after.	10 months after.	14 months after.
Litmus ...	Unbleached.	Unbleached.	Unbleached.	Unbleached	Unbleached colour slightly purplish.	Unbleached colour slightly purplish.	Began to bleach after few days, after 2 months quite bleached.	Bleached.	Bleached.
Methyl Blue ...	”	”	”	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Colour still strong.	Colour still strong.
Methyl Green ...	Solution almost colourless with black deposit. Sol. in HCl. giving green colour.	”	”	Unbleached.	Unbleached.	Unbleached.	Changed to a deep bluish black muddy fluid.	”	”
Methyl Orange ...	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Dried up.	
Eosine ...	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Still strong coloured.	Decided bleaching.	Decided bleaching but not complete.	Very small amount of colour left.

C. *All colours in solution in water, placed in tubes drawn out and connected with Sprengel Pump, solutions then boiled for 15 minutes, after which the tubes were completely exhausted while liquids were hot, and then hermetically closed.*

Colour.	In Total Darkness.			In Diffused Daylight opposite a North Window.				Exposed Daily to Direct Sunlight.			
	2 months after.	10 months after.	14 months after.	2 months after.	10 months after.	14 months after.	35 months after.	2 months after.	10 months after.	14 months after.	35 months after.
Litmus	Unbleached	Unbleached	Unbleached	Unbleached	Very slightly bleached	Very slightly bleached	Practically unbleached	Apparently slight diminution in colour.	Slightly bleached	Only partially bleached	Only partially bleached
Methyl Blue ...	”	”	”	”	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached
” Green ...	”	”	”	”	”	”	”	”	”	”	”
” Orange ...	”	”	”	”	”	”	”	”	”	”	”
Eosine	”	”	”	No practical bleaching action.	No practical change.	No practical change.	No practical change.	No practical bleaching action.	No practical change.	No practical change.	No practical change.
Rosaniline Acetate ...	”	”	”	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached	Unbleached

D. *Cotton-wool dyed with strong solutions of colours, and dried carefully, placed in test tubes plugged with cotton-wool, exposed therefore freely to air in ordinary hygrometric conditions.*

Colour.	In Total Darkness.			Exposed Daily to Direct Sunlight.		
	2 months after.	10 months after.	14 months after.	2 months after.	10 months after.	14 months after.
Litmus	Unbleached.	Unbleached.	Unbleached.	Largely bleached.	Entirely bleached.	Entirely bleached.
Methyl Blue	"	"	"	Bleached considerably.	"	"
" Green	"	"	"	Largely bleached.	"	"
" Orange	"	"	"	"	"	"
Eosine	"	"	"	Almost entirely bleached.	"	"
Rosaniline Acetate	"	"	"	Commencing to bleach.	"	"

E. *Cotton-wool dyed with strong solutions of colours, then dried thoroughly and placed in tubes which were rendered vacuous by Sprengel Pump, and the tubes then hermetically sealed.*

Colour.	In Total Darkness.				Exposed Daily to Direct Sunlight.			
	2 months after.	10 months after.	14 months after.	35 months after.	2 months after.	10 months after.	14 months after.	35 months after.
Litmus	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Still strongly coloured.	Still rather strongly coloured, but less so than when started.	Considerably bleached but still has light blue colour.	Considerably bleached but still has faint colour.
Methyl Blue ...	,,	,,	,,	,,	Apparently slight tendency to bleaching in parts.	Slight tendency to bleaching, colour not so brilliant.	Slight tendency to bleaching.	Still strongly coloured.
,, Green ...	,,	,,	,,	,,	Considerably bleached.	Considerably bleached.	Practically entirely bleached.	Practically bleached.
,, Orange ...	,,	,,	,,	,,	,,	Distinctly bleached.	Entirely bleached.	Bleached.
Eosine	,,	,,	,,	,,	Very decided bleaching.	Almost entirely bleached.	Practically entirely bleached.	Bleached.
Rosaniline Acetate ...	,,	,,	,,	,,	Unbleached.	Unbleached.	Unbleached.	Unchanged.

F. *Asbestus ignited for an hour to a full red heat and then cooled and dyed with strong solutions of various colours and dried. Samples placed in test tubes, the mouths of which were simply plugged with cotton-wool.*

Colours.	In Total Darkness.				Exposed Daily to Direct Sunlight.			
	2 months after.	10 months after.	14 months after.	35 months after.	2 months after.	10 months after.	14 months after.	35 months after.
Litmus	Unbleached.	Unbleached.	Unbleached.	Unbleached.	Considerably bleached.	Entirely bleached.	Entirely bleached.	
Methyl Blue ...	,,	,,	,,	,,	Almost unchanged.	Almost unchanged.	Almost unchanged.	Very little changed.
,, Green ...	,,	,,	,,	,,	Partially entirely bleached.	Entirely bleached.	Entirely bleached.	
,, Orange ...	This colour does not dye Asbestus at all well. Hence no experiments were made.							
Eosine	Unbleached.	Unbleached.	Unbleached.	Unbleached	Almost bleached.	Practically bleached.	Entirely bleached.	
Rosaniline Acetate ...	,,	,,	,,	,,	,,	,,	Bleached.	Bleached.

G. *Asbestus ignited for an hour to a full red heat and then cooled and dyed with strong solutions of various colours and dried. Samples placed in tubes, exhausted by Sprengel Pump and then sealed hermetically.*

Colours.	In Total Darkness.				Exposed Daily to Direct Sunlight.			
	2 months after.	10 months after.	14 months after.	35 months after.	2 months after.	10 months after.	14 months after.	35 months after.
Litmus...	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached
Methyl Blue	„	„	„	„	„	„	„	„
„ Green	„	„	„	„	Small amount of bleaching	Slight amount of bleacbing	Slight bleaching action	Still strongly coloured
„ Orange	This colour does not dye Asbestus. Experiments therefore not tried.							
Eosine	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached	Un-bleached
Rosaniline Acetate... ...	„	„	„	„	Colour not quite so brilliant but no bleaching.	Colour not quite so brilliant but not bleached.	Colour not quite so brilliant.	Still very strongly coloured.

The general results shown in the foregoing seven tables may be fairly accurately summarized in the following small table.

General results of experiments on the bleaching action of Sunlight on Colours.

	In Darkness.	In Diffused Day-light.	In Sun-light.
Solution of colours exposed to air. Solution unboiled...	Unbleached	Unbleached	All bleached
,, ,, ,, ,, boiled ...	,,	,,	Partial bleaching.
,, in vacuô ,, ...	,,	,,	Unbleached
Colours on cotton-wool *in air*, in ordinary hygrometric state	,,	,,	Bleached
,, ,, in vacuô	,,	,,	Partial bleaching.
,, on asbestus *in air*, in ordinary hygrometric state	,,	,,	Bleached
,, ,, in vacuô	,,	,,	Unbleached

The following general conclusions appear to follow from the above experiments taken in conjunction with a number of others which cannot be described in detail :—

1. Organic colours, both in solution in water or on dyed fabrics inorganic or organic, exposed freely to the action of air in the presence of the usual atmospheric conditions of moisture, etc., are practically unacted on in darkness even when exposed to these conditions for nearly three years.

2. Organic colours in the conditions mentioned in 1, are also practically unaffected by diffused daylight opposite a north window, even for the same period of nearly three years.

3. Organic colours in the conditions mentioned in 1, when exposed to the direct rays of the sun are all bleached, but with varying rapidity.

4. In the absence of air (moisture, etc.) strong sunlight, even for a period of three years, has practically no bleaching action on organic colours either in solution in water or used as dyes on inorganic fabrics. In the case of organic fabrics partial bleaching occurs.

5. It hence follows from 4 that the bleaching is not due to any action of light alone or to any volatility of the colouring matters.

6. The bleaching of colours takes place less rapidly when the colours are in solution than when they are dyed on fabrics.

7. The bleaching of colours in solution takes place less rapidly if the living germs or organisms in the solutions are destroyed by boiling than if they be not so destroyed.

8. The bleaching action of light appears to be more powerful if the colours are in contact with an organic fabric than if they are used to colour inorganic materials (asbestus).

9. The bleaching action of light in presence of air is much facilitated by the presence of moisture in contact with the colours and more particularly of *evaporating* water in contact with dyed fabrics.

10. There can therefore be little doubt that the bleaching action of light on ordinary organic colouring matters is usually due to oxidation. This oxidation when facilitated by evaporating water is probably or almost certainly due to the action of ozone, for Gorup von Besanez has shown that ozone is invariably formed when water evaporates in the air.* It therefore appears highly probable also that the action of the sunlight on the oxygen of the air *brings it into an active condition* (resembling perhaps that of ozone), and that the bleaching of organic colours is due to oxidation from this cause; for ordinary oxygen uninfluenced by sunlight does not bleach.

No. 3. *Notes on, and drawings of, the animals of various Indian Land Mollusca (Pulmonifera).*—*By* LIEUT.-COLONEL H. H. GODWIN-AUSTEN, F.R.S., F.Z.S., &c.

[Read 3rd April.]

Plate VII.

Continued from J. A. S. B., Pt. ii., Vol. LI, 1882, *p.* 71.

After the long lapse of 12 years since publishing my second paper (in 1882), on the drawings of Indian Land-Mollusca made by native artists under the superintendence of Ferdinand Stoliczka, I now forward a third, with the hope that it will lead some of our younger naturalists to make notes and drawings, and if possible dissections, of Indian species, so that they may be more accurately placed in generic position.

The first I have to notice and reproduce on Plate vii, fig. 1, is No. 29 of Ferd. Stoliczka's drawings, a very careful and accurate one of *Helix octhoplax*, with his MS. note attached,—"Asalu; sent down by Major Godwin-Austen." In 1869 I was surveying in the Naga Hills and

* Ann. Chem. Pharm. clxi. 232; also Roscoe and Schorlemmer Treatise on Chemistry Vol. I., p. 200.